



Steam reforming of ethanol–phenol mixture on Ni/Al₂O₃: Effect of Ni loading and sulphur deactivation

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ABSTRACT

The steam reforming of ethanol/phenol mixture (168 g_{TOT}/Nm³, ethanol:phenol 2:1 mol, GHSV = 54,000 h⁻¹) assumed as a model for tar mixtures, has been studied over Ni/Al₂O₃ catalysts. The effects of reaction temperature, Ni loading (from 0 to 39 (wt%/wt%)) and of the presence of sulphur has been investigated. If sufficiently charged with Nickel (e.g. 39% Ni with 107 m²/g surface area), Ni/Al₂O₃ catalysts are effective in complete steam reforming of the tar model molecules at 873 K, with CO₂ as the main C-containing reaction product and H₂ yield of 85%. The 5% Ni/Al₂O₃ can also produce the complete destruction of the molecules but at 973 K. These catalysts do not deactivate significantly by coking in the timescale of some hours at 873–1023 K. Starting with unreduce catalysts, a conditioning effect is evident on stream, supposed to be associated to the formation of “optimal” nickel metal particles. At lower temperatures the steam reforming activity towards phenol + ethanol mixture vanishes, with the appearance of reactions producing ethylene, acetaldehyde, and mono- and di-alkyl-phenols. Working at 973 K, all Ni/Al₂O₃ catalysts are strongly deactivated by 210 ppm of tetrahydrothiophene. However, catalytic activity is recovered by flowing with sulphur-free steam reforming feed, although the CO₂/CO product ratio, and consequently also the final hydrogen yield, is permanently altered. It is proposed that the last reaction step, i.e. the oxidation of adsorbed CO to CO₂ previous of its desorption, involves isolated cationic Ni centres that are irreversibly deactivated by sulphur or during the poisoning/regeneration cycle.

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1. Introduction

Different technologies are currently under development to produce biofuels, in order to reduce greenhouse gas emissions and dependence from fossil fuels [1]. Gasification of biomasses represents a promising and already quite established approach to produce syngases [2], whose combustion or conversion may give rise to renewable energy, bio-hydrogen and liquid biofuels. However, gasification technologies present a number of drawbacks, among which the production of tar [3] (1–50 g/Nm³ depending mainly on the reactor type) and the presence of sulphur (20–600 ppmv H₂S depending on the biomass [4]) and chlorine (up to some hundreds of ppm depending on the biomass [5]) as pollutants of the resulting syngas. Biomass tar is a complex mixture of quite heavy organic molecules produced together with other low volatility oxygenates [6]. These molecules can condense in the cold sections of the plant (like on heat exchangers) producing fouling, or

may cause coking and deactivation of catalysts (such as for water gas shift) and anodes of fuel cells [7].

Several approaches have been proposed to purify biomass-derived syngases from tar. Catalytic steam reforming (SR) appears to be one of the most interesting approaches, being performed nearly at the same temperature of syngas coming out from the reactor. Ni-based SR catalysts similar to those used for methane SR [8] appear to be active but noble metal based catalysts are even more active, less prone to coking and sulphur resistant [9,10]. Although catalysts specific for biomass tar SR, apparently based on Nickel [11], are commercialized, most of the data available in the literature concern either home-made catalysts or commercial catalysts optimized for natural gas reforming or pre-reforming. Indeed, it seems that consensus has still not been obtained on the best composition and characteristics of catalysts optimized for biomass tar SR. On the other hand, although data are available for treatment of real biosyngases in pilot plants [12–14], most laboratory experiments for tar SR are carried out using one of the most abundant tar molecules such as either an aromatic hydrocarbon (benzene, toluene, and naphthalene) or phenol, which is reported to be the most abundant tar species after low temperature biomass gasification [15]. However, several organic molecules are present together

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Table 1
Properties of the catalysts.

Notation	NiO loading (wt%)	Ni loading (wt%)	$m^2_{\text{CAT}}/at_{\text{Ni}} [\times 10^{-20}]$	$m^2_{\text{SUP}}/at_{\text{Ni}} [\times 10^{-20}]$	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore sizes (nm)	NiO crystal size (nm)
Ni0 (Siralox 5/170)	0	0	–	–	172	0.49	10.1	–
Ni5	6	5	31.7	35.2	155	0.45	9.9	n.d.
Ni16	20	16	9.7	12.2	137	0.35	9.0	~10
Ni39	50	39	3.7	6.0	107	0.26	8.0, 4.5	~25

within tar, and the possibility of their mutual reaction has usually not been considered.

The SR of phenol has been investigated both as a model of tar SR and as a model of bio-oil SR, another route to “bio-syngases” and “bio-hydrogen” [16]: in fact bio-oils, i.e. the liquids produced by biomass pyrolysis, are rich in phenols, together with several other aliphatic and aromatic oxygenates and hydrocarbons. Rioche et al. [17] tested separately SR of phenol and ethanol, and of other model molecules for bio-oils, over noble metal catalysts (Pt, Pd and Rh) supported on alumina and ceria–zirconia, concluding that Rhodium gives rise to most active catalysts for both molecules. Matas Guell et al. studied Ni supported on lanthana–zirconia and ceria–zirconia for phenol SR [18] and found them active and only slowly deactivated at 973 K. The groups of Efstatthiou and Fierro investigated phenol SR over cheap mineral powders (like calcite, dolomite and olivine, that can be introduced into the gasification reactor system [19]), as well as over Iron- [20] and Rhodium-based catalysts [21]. In the last paper these authors reported that optimized Rh-based catalysts are more active than commercial Ni/Al₂O₃ based catalyst at low temperature (≤ 773 K), when conversion is still incomplete, while commercial Ni/Al₂O₃ based catalyst is more active at 823 K.

However, performing tar SR at temperatures significantly lower than those of the syngas coming out from the gasification reactor (usually 873–1173 K depending on reaction configuration) may be not practical, depending on the reactor configuration. In fact at low temperature SR reactions become thermodynamically less favoured, methanation becoming favoured and occurring on metal catalysts, while de novo formation of heavy molecules can also take place at least on Ni-based catalysts [22]. These catalysts can be useful when activity at very low temperature is not necessary, stability with respect to sintering, coking, reoxidation [23] and deactivation by sulphur [24] and chlorine being, however, relevant factors. Easy regeneration would also be a useful property. Indeed, the cited studies of phenol SR did not consider the effect of sulphur in the gas.

We investigated recently the SR of ethanol–phenol mixture over a 5% Ni–Al₂O₃ catalyst, in order to evaluate the activity of this material and the possible co-interaction between different molecules co-present in the syngas. We found indeed that at low temperature (720 K) this material catalyzes the alkylation of phenol by ethanol, while SR is total for both molecules to CO and CO₂ with small amounts of methane at 950 K [22]. In the present paper we will describe and discuss our results concerning the SR of ethanol–phenol mixtures, as a model for biomass tar, over Ni–Al₂O₃ catalysts considering the effects of reaction temperature (both by increasing and decreasing it), of Ni content, and of the presence of sulphur in the reactant mixture.

2. Experimental

2.1. Catalysts preparation

The support material used to prepare the catalysts is Siralox 5/170 from Sasol. The virtual composition of this support is 95% Al₂O₃, 5% SiO₂, with traces of iron and sodium as impurities. The presence of silica is useful to increase the stability of transitional

alumina towards phase transition. Ni–alumina catalysts (Table 1) have been prepared by wet impregnation using Ni(NO₃)₂·6H₂O water solution, followed by calcination at 973 K for 5 h.

2.2. Catalysts characterization

A modified Sartorius symmetrical microbalance, described elsewhere [25], was used for the determination of the specific surface area and of the pore size distribution. About 50 mg of powder was placed in a Pt crucible and introduced in the microbalance. Then the sample was dried at 383 K in vacuum (10^{-4} Pa) and, after the weight was stabilized at the microbalance sensitivity (0.01 mg), was cooled at 78 K without removing it from the crucible and without air contamination. N₂ gas was introduced step by step in the apparatus until a maximum relative pressure of 0.995. Adsorption–desorption isotherm was made by recording the increase–decrease of the sample weight at the different relative pressures.

The specific surface area was calculated applying the multi-point BET method [26]. The mesopore size distribution curve was obtained by using the desorption branch of the nitrogen isotherm, according the Orr–Dalla Valle method [27].

X-ray powder diffraction patterns have been carried out with a X-Pert Philips diffractometer using a Cu K α radiation.

2.3. Catalytic experiments

A tubular silica glass flow reactor, containing a fixed bed with 44.1 mg of catalyst mixed with 440 mg of silica glass particles 0.25–0.21 mm (corresponding to 60–70 mesh sieved) was fed with 40 Nml/min (GHSV = 54,000 h⁻¹) of a gaseous mixture 39.3% He, 54.6% water, 4.1% ethanol and 2% phenol mol/mol. For the thermal conversion experiment the bed was constituted by 484.1 mg of silica glass. A phenol–water–ethanol single phase liquid solution was pumped through a HPLC pump (Shimadzu Corp. LC-D10 AD) in an appropriate heating section at 583 K of the feed line to produce a gas whose composition corresponds to 168 g/Nm³ of ethanol + phenol (84.9 g/Nm³ of phenol), and 439 g/Nm³ water vapour in the He inert carrier. No catalyst pretreatments were performed. Reactor oven temperature was varied from 773 K to 1023 K, and vice versa. The measured bed temperature was slightly lower than the furnace temperature according to the whole endothermicity of the reactions. The evaluation of activation energies during partial reactants conversion at low temperature 573–773 K allowed us to exclude at least in this temperature region significant diffusion limitations.

In order to reveal conditioning effect catalytic experiments were performed both rising and reducing reaction temperature (773 K, 873 K, 973 K, 1023 K and reverse).

To investigate sulphur poisoning tetrahydrothiophene (C₄H₈S, THT) was used as a contaminant of the feed. In one series of experiments performed at 973 K 210 ppm of THT were continuously fed with the reactants, to whose solution liquid THT was previously mixed, by increasing time on stream up to 6 h.

In another series of experiments, also performed at 973 K, the effects of two sequential pulses of THT (first 0.011 mol_S/mol_{Ni} and after 0.033 mol_S/mol_{Ni}) and of a further stay on the sulphur-free stream on the catalytic activity of the different catalysts were

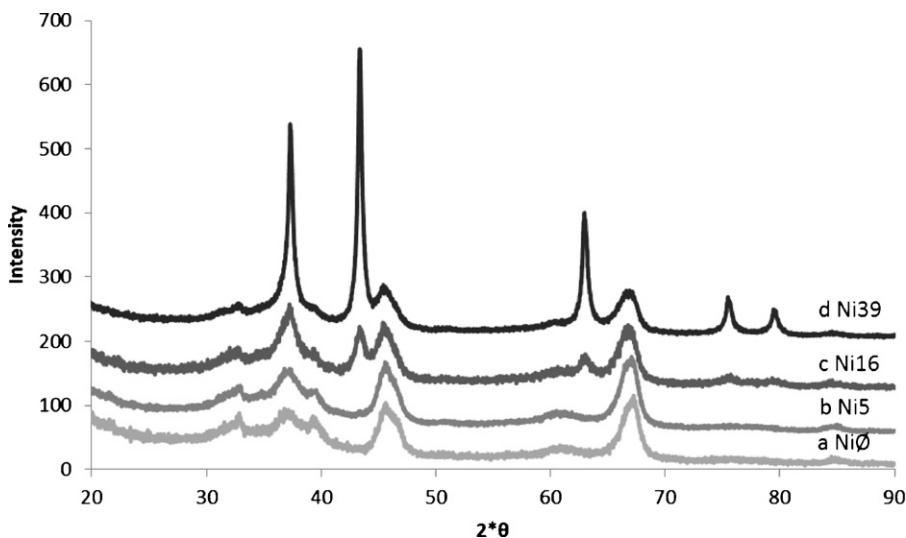


Fig. 1. XRD diffraction patterns of the catalysts (Cu K α radiation).

studied. In this case the THT have been pulsed injecting, with a syringe, the corresponding quantity of liquid in the preheating zone.

Neither THT nor any other sulphur compounds can be detected by GC nor GC-MS, due to their small concentration. IR experiments show that THT sulphidizes the catalysts producing gas-phase butene.

Product analysis was performed with a GC/MS (Focus-ISQ Thermoscientific), in order to have a precise identification of the compounds, and with a gas-chromatograph Agilent 4890 equipped with a Varian capillary column "Molsieve 5A/Porabond Q Tandem" and TCD and FID detectors in series. Between the detectors, a nickel catalyst tube was employed to reduce CO and CO₂ to CH₄. The sampling of the outlet vapours was made by injection, using a gas-tight syringe with a nominal volume of 0.25 ml. A sampling injection point at the end of the vapourization zone allowed us to analyse the reactants and to determine that the feed composition was not modified in this section. Hydrogen was detected as a negative peak in the TCD detector signal of GC and also calculated on the basis of the C-product yields. The two measures were confirmed to be in reasonable agreement.

Analyses were performed when apparent steady state conditions was reached, generally in 1 h. Reactants conversion is defined as follows:

$$X_{\text{reactant}} = \frac{n_{\text{react in}} - n_{\text{react out}}}{n_{\text{react in}}} \quad (1)$$

while selectivity to product i is defined as follows:

$$S_i = \frac{n_i}{v_i(n_{\text{react in}} - n_{\text{react out}})} \quad (2)$$

where n_i is the moles number of compound i , and v_i is the ratio of stoichiometric reaction coefficients. When applied to the overall carbon feed, n_i is the carbon moles number of compound i , n_{react} is the carbon moles number of reactants mixture as a whole and $v_i = 1$.

3. Results

3.1. X-ray diffraction study

XRD pattern of the Siralox support (Fig. 1a) shows the peaks typical of a transition alumina. The incomplete splitting of the

two most intense peaks (near $2\theta = 67^\circ$ and 46°) which are usually assigned to 440 and 400 spinel type crystal planes, as well as the observation of additional weak peaks (e.g. at $2\theta = 51^\circ$) evidence an evolution of the structure from the pure γ -Al₂O₃ phase (cubic defective spinel) to the tetragonal structure such as δ -Al₂O₃ or γ' -Al₂O₃ [28]. The pattern of the support is perhaps slightly modified with a small increase of the tetragonal deformation by Nickel loading (Fig. 1b-d). No other peaks are observed for Ni5 while for samples Ni16 and Ni39 characteristic peaks of the NiO phase (rock salt or periclase structure) appear. The analysis of the crystal size of the nickel oxide phase through the Scherrer calculation gives rise to values lower than 50 nm in both cases, of the order of ca. 10 nm for Ni16 and 25 nm for Ni39.

3.2. Effect of Ni loading on catalyst morphology

In Fig. 2, left section, the nitrogen adsorption and desorption isotherms, recorded gravimetrically at 78 K, of all catalytic materials are reported. All four adsorption isotherms can be classified as type IV following the Brunauer classification. Adsorption and desorption isotherms provide evidence, in all cases, of the presence of cylindrical micropores according to the parallelism of the branches forming the hysteresis loops. On the other hand, the decrease of the total nitrogen adsorbed amount by increasing nickel loading provides evidence of the decrease of the total pores volume and surface area. The pore size distributions of the four samples, reported in right part of Fig. 2, show the predominance of a single family of pores characterized by a size of near 10 nm, while for Ni16 and Ni39 a clear progressive shift to lower pore size is evident (down to 8 nm). For Ni39 a second family of pores becomes well distinguishable, with a pore size of 4.5 nm. The surface areas measured through the BET equation [26] progressively decrease from 172 m²/g for NiØ to 107 m²/g for Ni39 (Table 1). Both considering the area of the support and that of the catalysts, the surface density of Ni atoms (calculated in Table 1) may be considered to be well lower than that needed to cover the surface with a theoretical monolayer for Ni5. Thus in the case of Ni5 alumina uncovered surface would certainly exist. The surface density of Ni calculated for Ni16, near 10 Å² per Ni atom, is likely similar to that needed to cover the all surface, while for Ni39, the value of 3 Å² per Ni atom indicates that, by theory, the theoretical monolayer coverage is exceeded. However, the detection of NiO particles by XRD indicates that,

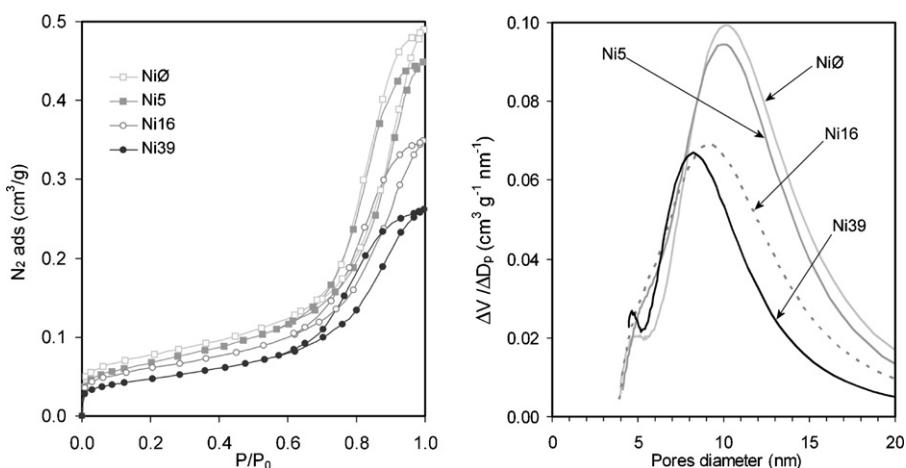


Fig. 2. Nitrogen adsorption isotherms at 77 K and pore size distributions.

Table 2

carbon and reactants conversions (X_i) and carbon based selectivities to products (S_i) on phenol–ethanol–water reaction on pure silica glass bed.

T furnace (K)	Experiment on silica glass bed										
	C conversion	$X\text{C}_2\text{H}_6\text{O}$	$X\text{C}_6\text{H}_6\text{O}$	$X\text{H}_2\text{O}$	$Y\text{H}_2$	$S\text{CH}_4$	$S\text{CO}$	$S\text{CO}_2$	$S\text{CH}_2\text{CH}_2$	$S\text{CH}_3\text{CHO}$	$S\text{C}_6\text{H}_6$
773	0.03	0.05	0.01	0.00	0.01	0.00	0.03	0.17	0.00	0.79	0.00
873	0.07	0.12	0.03	0.01	0.02	0.03	0.07	0.17	0.10	0.64	0.00
973	0.17	0.33	0.10	0.01	0.04	0.03	0.18	0.16	0.27	0.29	0.07
1023	0.43	0.68	0.27	0.03	0.09	0.43	0.22	0.11	0.28	0.20	0.09
973	0.22	0.35	0.14	0.03	0.07	0.04	0.20	0.16	0.19	0.36	0.05

also for Ni16 and Ni39 the alumina surface may be uncompletely covered.

3.3. Catalytic activity on sulphur free stream

In Table 2 the results of the blank experiment performed with silica glass particles only in the bed are reported. The conversion of reactants is very small at 773 and 873 K with the formation of acetaldehyde and CO_2 as the main products. Only at 1023 K a significant but still largely partial conversion is obtained: ethylene and acetaldehyde are the main ethanol decomposition products (with selectivity to ethylene increasing and selectivity to acetaldehyde decreasing by increasing reaction temperature) while phenol is mainly converted into CO, CO_2 and benzene.

In Fig. 3 the hydrogen yields obtained during the reaction over the different catalysts are compared. This figure allows us to have a comprehensive picture of the main catalytic behaviour. However the catalytic system under investigation is really complex thus the behaviour of the single catalyst in each experiment will be discussed in detail hereinafter.

In Table 3 the catalytic behaviour of pure Siralox support (NiØ) is summarized. The conversion of ethanol on alumina is complete already at 773 K mostly producing ethylene while alkylation of phenol to mono and di alkylphenols is also already significant. By increasing reaction temperature the conversion of both reactants tend to decrease while selectivities to acetaldehyde, methane, benzene and CO grow. In the experiment performed by decreasing reaction temperature, conversion continues to decrease

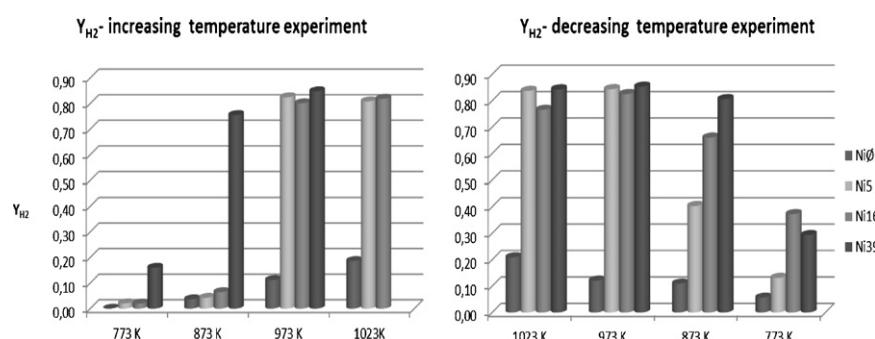


Fig. 3. Hydrogen yields on the different catalysts tested in function of temperature.

Table 3carbon and reactants conversions (X_i) and carbon based selectivities to products (S_i) on phenol–ethanol–water reaction on NiØ catalyst.

T furnace (K)	Increasing temperature experiment on NiØ									
	C conversion			X C ₂ H ₆ O		X C ₆ H ₆ O		X H ₂ O		Y H ₂
773	0.66			1.00		0.25		-0.08		-0.00
873	0.52			1.00		0.17		-0.06		0.04
973	0.34			0.63		0.05		-0.01		0.11
1023	0.33			0.74		0.08		-0.01		0.19
	S CH ₄	S CO	S CO ₂	S CH ₂ CH ₂	S CH ₃ CH ₃	S CH ₃ CHO	S CH ₃ COCH ₃	S C ₆ H ₆	S C ₈	S C ₁₀
773	0.00	0.00	0.01	0.66	0.03	0.06	0.00	0.00	0.14	0.09
873	0.01	0.01	0.02	0.63	0.00	0.10	0.00	0.01	0.18	0.05
973	0.08	0.11	0.05	0.36	0.03	0.28	0.00	0.04	0.05	0.00
1023	0.09	0.18	0.06	0.32	0.00	0.18	0.03	0.15	0.00	0.00
Decreasing temperature experiment on NiØ										
	C conversion			X C ₂ H ₆ O		X C ₆ H ₆ O		X H ₂ O		Y H ₂
	1023	0.36		0.78		0.08		0.00		0.21
973	0.24			0.46		0.05		0.00		0.12
873	0.14			0.33		0.01		0.01		0.11
773	0.06			0.15		0.00		0.01		0.06
	S CH ₄	S CO	S CO ₂	S CH ₂ CH ₂	S CH ₃ CH ₃	S CH ₃ CHO	S CH ₃ COCH ₃	S C ₆ H ₆	S C ₈	S C ₁₀
1023	0.09	0.17	0.08	0.29	0.00	0.23	0.00	0.14	0.00	0.00
973	0.07	0.13	0.08	0.23	0.00	0.38	0.00	0.11	0.00	0.00
873	0.02	0.05	0.13	0.09	0.00	0.66	0.00	0.05	0.00	0.00
773	0.00	0.00	0.16	0.00	0.00	0.84	0.00	0.00	0.00	0.00

while acetaldehyde becomes the more important product at 773 K. The catalytic activity of the alumina bed after the entire experiment seems to be quite comparable to that of the blank experiment with poor conversion and high selectivity to acetaldehyde. It is evident that the alumina bed is deactivated, very likely by coking, at temperatures above 773 K. Clean alumina at 773 K is active as a dehydration and alkylation catalyst, as expected.

The production of alkylphenols accounts for phenol conversion at 773 K, in the increasing temperature experiment. GC/MS analysis allows us to reveal o-ethylphenol to be the most abundant monoalkylation product (about 76% among monoalkylphenol isomers) and also the formation of non-negligible amounts of dialkylphenols, about 34% among total alkylates.

In Table 4 the catalytic behaviour of Ni5 catalyst is reported. The behaviour of this catalyst at 773 K and 873 K in the increasing temperature experiment is similar to that of pure alumina, although with slightly lower phenol alkylation activity. Ethylene is the predominant product of ethanol conversion at these temperatures, with small amounts of acetaldehyde, while alkylates account again for small phenol conversion at 773 K. Ethylphenol distribution is slightly different here than for NiØ catalyst: o-ethylphenol is near 50% of all monoalkylates, dialkylates are near 20% of all alkylphenols and significant amount of 1-ethyl-3,4-dimethylphenol is also revealed (9% of all alkylphenols). At 873 K phenol conversion slightly decreases, alkylation almost vanishes and small amounts of CO and CO₂ appear among the products suggesting that SR of both reactants starts to occur.

At 973 K the catalytic behaviour of Ni5 fully changes: both phenol and ethanol are fully converted to CO₂, CO and traces of methane. Thus dehydration, dehydrogenation/hydrogenation and alkylation fully disappear while only SR of both reactants occurs. By further increasing reaction temperature up to 1023 K the only modification observed is a slight increase of CO selectivity with corresponding decrease of both CO₂ and CH₄ selectivities.

Experiments of catalytic conversion on Ni5 catalyst have also been performed by decreasing reaction temperatures from 1023 K to 773 K. The first experiment performed at the highest

temperature confirms that performed at the same temperature (1023 K) as the last experiment in the increasing temperature sequence. The only difference is the full absence of CH₄ observed now. By reducing temperature to 973 K methane production is still zero while the ratio CO₂/CO does not change with respect to the higher temperature experiment, in contrast to what happened in the increasing temperature sequence. At 873 K phenol conversion drops to 47% and ethylene, ethane, methane and benzene are observed as minor byproducts while CO₂/CO ratio increases.

With respect to the experiment performed at the same temperature in the increasing temperature sequence, this experiment shows much higher SR of both reactants, accordingly much higher conversion of phenol and much less selectivity to products different from CO and CO₂ (ethylene and acetaldehyde primarily) by converting ethanol.

The same experiments have been performed with the Ni16 catalyst (Table 5). The behaviours of Ni5 and Ni16 at 773 K are quite similar. Ethanol is almost totally converted mainly to ethylene (65% selectivity with respect to ethanol) while conversion of phenol is 27% full to alkylates. Ethanol conversion also produces acetaldehyde (16% selectivity) and alkylates. By increasing temperature to 873 K the production of alkylates and ethylene decreases while carbon oxides start to be observed while ethane (13% selectivity on ethanol basis) and acetaldehyde are also produced. This behaviour shows that SR starts at this temperature over this catalyst, hydrogen being partially consumed producing ethane. At 973 K and above SR is the largely predominant reaction with almost total conversion of both reactants and production of CO, CO₂ and traces of methane.

In the experiments performed by decreasing reaction temperature full conversion of both organic reactants to SR products is observed at 1023 K and 973 K while at 873 K conversions still approach unit, but small amounts of ethane, ethylene, benzene and methane are also produced and the CO₂/CO ratio increases significantly. At 773 K SR still predominates but phenol conversion falls down to 20%, alkylates accounting for 33% of it, while ethylene accounts for 19% of ethanol conversion. The difference in the behaviour of the catalyst at 873 K in the increasing and decreasing

Table 4carbon and reactants conversions (X_i) and carbon based selectivities to products (S_i) on phenol–ethanol–water reaction on Ni5 catalyst.

T furnace (K)		Increasing temperature experiment on Ni5									
		C conversion		$X C_2H_6O$		$X C_6H_6O$		$X H_2O$		$Y H_2$	
773		0.74		1.00		0.17		-0.07		0.02	
873		0.64		1.00		0.13		-0.04		0.04	
973		1.00		1.00		1.00		0.49		0.82	
1023		1.00		1.00		1.00		0.46		0.81	
	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S HCHO$	$S CH_3CHO$	$S CH_3COCH_3$	$S C_6H_6$	$S C_7$	$S C_8$
773	0.01	0.00	0.02	0.81	0.01	0.01	0.08	0.01	0.01	0.00	0.05
873	0.01	0.03	0.03	0.70	0.06	0.00	0.14	0.00	0.01	0.01	0.00
973	0.04	0.30	0.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1023	0.02	0.40	0.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Decreasing temperature experiment on Ni5											
		C conversion		$X C_2H_6O$		$X C_6H_6O$		$X H_2O$		$Y H_2$	
1023		1.00		1.00		1.00		0.47		0.84	
973		1.00		1.00		1.00		0.48		0.84	
873		0.68		1.00		0.47		0.20		0.40	
773		0.60		1.00		0.34		0.03		0.13	
	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S CH_3CHO$	$S C_6H_6$	$S C_8$	$S C_{10}$		
1023	0.00	0.41	0.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
973	0.00	0.39	0.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
873	0.02	0.24	0.45	0.21	0.03	0.00	0.03	0.02	0.00	0.00	
773	0.01	0.03	0.21	0.51	0.01	0.05	0.00	0.15	0.02		

Table 5carbon and reactants conversions (X_i) and carbon based selectivities to products (S_i) on phenol–ethanol–water reaction on Ni16 catalyst.

T furnace (K)		Increasing temperature experiment on NM6								
		C conversion		$X C_2H_6O$		$X C_6H_6O$		$X H_2O$		$Y H_2$
773		0.55		0.98		0.27		-0.05		0.02
873		0.55		0.86		0.25		-0.01		0.06
973		0.95		0.98		0.93		0.46		0.80
1023		0.99		1.00		0.98		0.46		0.82
	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S CH_3OH$	$S CH_3COH$	$S C_6H_6$	$S C_8$	$S C_{10}$
773	0.00	0.00	0.01	0.46	0.00	0.01	0.11	0.00	0.36	0.05
873	0.01	0.09	0.13	0.40	0.10	0.00	0.13	0.01	0.14	0.00
973	0.01	0.36	0.59	0.00	0.00	0.00	0.03	0.00	0.00	0.00
1023	0.00	0.43	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Decreasing temperature experiment on Ni16										
		C conversion		$X C_2H_6O$		$X C_6H_6O$		$X H_2O$		$Y H_2$
1023		1.00		1.00		1.00		0.40		0.77
973		1.00		0.96		1.00		0.47		0.83
873		0.94		1.00		0.90		0.39		0.66
773		0.51		0.98		0.20		0.18		0.37
	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S CH_3CHC$	$S C_6H_6$	$S C_7$	$S C_8$	$S C_{10}$
1023	0.00	0.60	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00
973	0.02	0.39	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00
873	0.05	0.27	0.57	0.05	0.04	0.00	0.02	0.00	0.01	0.00
773	0.02	0.05	0.62	0.14	0.02	0.03	0.02	0.00	0.00	0.10

temperature experiment provide evidence of some kind of conditioning of the catalyst during higher temperature operations, we will discuss later on.

The experiment performed with Ni39 catalyst (Table 6) shows that, by increasing reaction temperature, SR occurs at a significant extent already at 773 K although conversion of both reactants is far from complete. In fact only 18% of phenol is converted, but it gives rise to CO and CO_2 for 88%, the rest being mostly constituted by alkylation products. Ethanol conversion is more than 90%, giving rise to ethylene, ethane, acetaldehyde, alkylates and SR products ($CO + CO_2$ represent the 14% of converted ethanol). At 873 K

conversion of both reactants is complete and SR is largely predominant with only traces of methane, ethylene, ethane and benzene. At 973 K complete SR occurs.

By decreasing reaction temperature SR is found complete at 1023 K, 973 K and 873 K, while at 773 K phenol conversion fell down to 41% and alkylates and ethylene, ethane and acetaldehyde are found among the products. Nevertheless at 773 K the conversion and the SR activity found in the decreasing temperature experiment are higher than in the increasing temperature experiment, showing again some kind of catalyst conditioning.

Table 6carbon and reactants conversions (X_i) and carbon based selectivities to products (S_i) on phenol–ethanol–water reaction on Ni39 catalyst.

T furnace (K)	Increasing temperature experiment on Ni39								
	C conversion		$X C_2H_6O$		$X C_6H_6O$		$X H_2O$		$Y H_2$
773	0.47		0.90		0.18		0.05		0.16
873	0.98		1.00		0.96		0.42		0.76
973	1.00		1.00		1.00		0.49		0.85
$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S HCHO$	$S CH_3COH$	$S C_6H_6$	$S C_8$	$S C_{10}$
773	0.01	0.06	0.25	0.30	0.01	0.00	0.32	0.00	0.02
873	0.04	0.37	0.55	0.02	0.01	0.00	0.00	0.01	0.00
973	0.01	0.37	0.63	0.00	0.00	0.00	0.00	0.00	0.00
Decreasing temperature experiment on Ni39									
C conversion		$X C_2H_6O$		$X C_6H_6O$		$X H_2O$		$Y H_2$	
1023	1.00		1.00		1.00		0.48		0.84
973	1.00		1.00		1.00		0.49		0.85
873	1.00		1.00		1.00		0.49		0.81
773	0.65		1.00		0.41		0.13		0.29
$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S CH_3CHO$	$S C_6H_6$	$S C_8$	$S C_{10}$	
1023	0.00	0.40	0.60	0.00	0.00	0.00	0.00	0.00	0.00
973	0.00	0.37	0.63	0.00	0.00	0.00	0.00	0.00	0.00
873	0.06	0.27	0.67	0.00	0.00	0.00	0.00	0.00	0.00
773	0.02	0.04	0.42	0.24	0.02	0.06	0.01	0.14	0.04

The analysis of the data discussed above indicates that the three Nickel containing catalysts give rise, in our condition, to complete SR of both reactants at 973 K and above. At lower temperatures all catalysts give rise to SR products (CO, CO_2 and small amounts of CH_4) together with other reaction products (ethylene, ethane, acetaldehyde benzene and alkylates products). The balance SR versus other reactions is shifted towards SR the more the higher the Ni content is and more in the experiments performed in decreasing reaction temperature than in those performed by increasing T. The “conditioning” effect (the increase of the SR activity at 773 K and 873 K as a result of a previous test at 1023 K and 973 K) appears to be most prominent for Ni16 catalyst.

3.4. Effect of sulphur on catalytic activity

To study the effect of sulphur on catalytic activity the reaction temperature of 973 K has been chosen; in fact at this temperature with sulphur free feed all three Ni containing catalysts give rise to total conversion to SR products.

All three catalysts (Table 7) modify their catalytic activity as an effect of prolonged exposition to the sulphur containing continuous feed. Catalysts deactivation is evident, resulting first in a drop of phenol conversion and in a shift of selectivity of ethanol conversion from carbon oxides towards ethylene, acetaldehyde and alkylates. This shift in the behaviour is evident near 300 min on stream after the introduction of THT in the liquid feed before the pump, for the three catalysts. An evaluation of the transient time of the HPLC pump allows us to conclude that catalytic activity is affected nearly 100 min after the beginning of real entrance of THT into the catalytic bed.

To differentiate the behaviour of the three catalysts with respect to sulphur poisoning we performed the experiments with pulse injections of the sulphur containing compound THT. On Ni5 catalyst (Fig. 4) the addition of 0.011 mol_S/mol_{Ni} (corresponding to 10.9 μg_S) pulse to the normal feed (performed 30 min before the product analysis) causes a decrease of phenol conversion down to 86% and a remarkable drop in the production of carbon dioxide with a corresponding increase in CO, methane, benzene and ethylene production. The further addition of 36.3 μg_S (ca. 0.033 mol_S/mol_{Ni}) again 30 min before product analysis, causes a further drop of

phenol conversion down to 33% and also a big decrease in the production of carbon oxides, together with a further increase in ethylene, acetaldehyde and benzene selectivities. Further contact of the catalyst with the sulphur free stream for 135 min results in the recovery of almost total conversion of both reactants through SR; however selectivity to CO is much higher than selectivity to CO_2 , in contrast to what was occurring before sulphur addition. Only small amounts of ethylene, ethane, methane and benzene are also produced. Further stay on sulphur free stream did not change very much the behaviour. These results provide evidence of a reversible deactivation of the SR activity by sulphur.

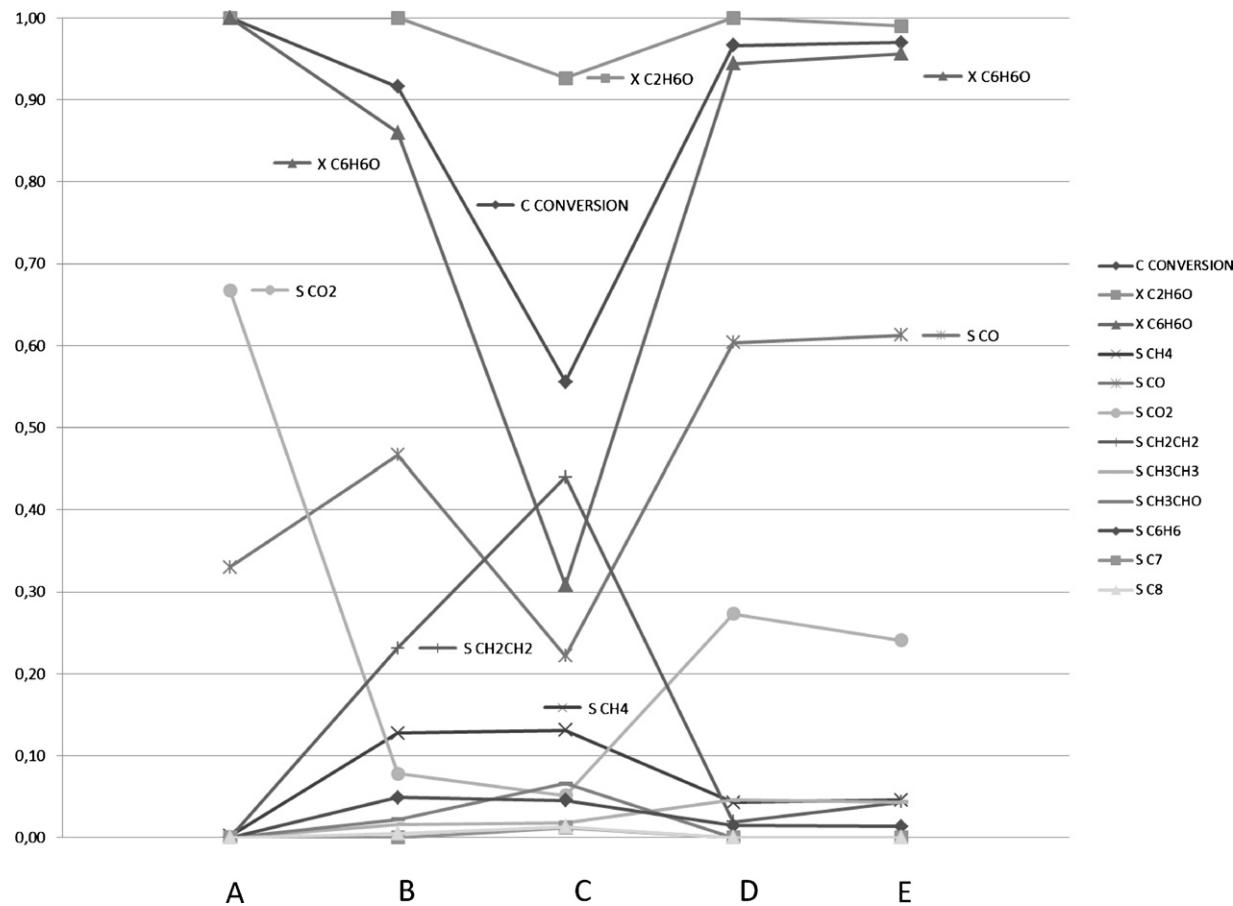
In contrast to what happens with Ni5 catalyst the addition of 0.011 mol_S/mol_{Ni} to the normal feed (performed 30 min before the product analysis) does not cause significant changes to the catalytic behaviour of Ni16 (Fig. 5). In this case 36.3 μg_S have been pulsed. The further addition of 0.033 mol_S/mol_{Ni}, i.e. 109 μg_S , causes an evident deactivation also of Ni16 catalyst. Phenol conversion drops to 19%, CO is produced more than CO_2 (again in contrast with what was occurring before sulphur addition) and ethylene is the main product of ethanol conversion, together with acetaldehyde and methane. Further stay on sulphur free stream causes recovering of the full conversion of both reactants through SR but CO is produced more than CO_2 and methane is produced in higher amount than usual (10% carbon selectivity).

The addition of 0.011 mol_S/mol_{Ni} (72.6 μg_S) causes a significant deactivation of Ni39 catalyst (Fig. 6) with a drop of both conversion of phenol (down to 60%) and of CO_2 selectivity (from 70% to 8%) and a concomitant increase in selectivities to ethylene (35%), benzene (15%) and methane (5%).

The further addition of 0.033 mol_S/mol_{Ni} (218 μg_S) causes a further deactivation of Ni39 catalyst: conversion of both reactants is reduced (80% for ethanol and 26% for phenol), CO selectivity decreases to 17% while predominant products are now ethylene (35%) and acetaldehyde (26%). Further stay on sulphur free stream results in a further progressive decrease of conversions of ethanol (to less than 70% after 212 min), phenol conversion being almost vanished, and in slight modification in products selectivities. In this case, however, we left the catalyst on He stream at r.t. overnight and we heated it again to 973 K in He and then feed was readmitted at 973 K. After 1 h the conversion of reactants was fully

Table 7carbon and reactants conversions (X_i) and carbon based selectivities to products (S_i) on phenol–ethanol–water reaction in the presence of THT 210 ppm.

	C conversion	$X C_2H_6O$	$X C_6H_6O$	$Y H_2$	$X H_2O$	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S CH_3COH$	$S C_6H_6$	$S C_7$	$S C_8$	
Ni5															
0 min	1.00	1.00	1.00	0.83	0.48	0.01	0.39	0.60	0.00	0.00	0.00	0.00	0.00	0.00	
90 min	0.94	0.98	0.92	0.81	0.46	0.01	0.36	0.63	0.00	0.00	0.00	0.00	0.00	0.00	
192 min	1.00	1.00	1.00	0.85	0.49	0.01	0.38	0.62	0.00	0.00	0.00	0.00	0.00	0.00	
292 min	0.81	0.95	0.66	0.14	0.05	0.11	0.23	0.07	0.39	0.05	0.04	0.09	0.01	0.01	
	C conversion	$X C_2H_5OH$	$X C_6H_6O$	$Y H_2$	$X H_2O$	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S HCHO$	$S CH_3OH$	$S CH_3CHO$	$S C_6H_6$	$S C_5H_6$
Ni16															
0 min	0.95	0.98	0.93	0.80	0.46	0.01	0.36	0.59	0.00	0.00	0.00	0.03	0.00	0.00	
89 min	1.00	1.00	1.00	0.84	0.48	0.01	0.39	0.60	0.00	0.00	0.00	0.00	0.00	0.00	
174 min	1.00	1.00	1.00	0.83	0.47	0.01	0.41	0.58	0.00	0.00	0.00	0.00	0.00	0.00	
251 min	1.00	1.00	1.00	0.84	0.48	0.01	0.38	0.61	0.00	0.00	0.00	0.00	0.00	0.00	
339 min	0.47	0.94	0.15	0.03	-0.02	0.09	0.14	0.05	0.46	0.02	0.05	0.00	0.14	0.05	0.01
	C conversion	$X C_2H_6O$	$X C_6H_6O$	$Y H_2$	$X H_2O$	$S CH_4$	$S CO$	$S CO_2$	$S CH_2CH_2$	$S CH_3CH_3$	$S CH_3CHO$	$S C_6H_6$	$S C_5H_6$	$S C_8$	
Ni39															
0 min	1.00	1.00	1.00	0.85	0.48	0.00	0.39	0.61	0.00	0.00	0.00	0.00	0.00	0.00	
90 min	1.00	1.00	1.00	0.85	0.49	0.01	0.37	0.62	0.00	0.00	0.00	0.00	0.00	0.00	
192 min	1.00	1.00	1.00	0.83	0.47	0.01	0.42	0.57	0.00	0.00	0.00	0.00	0.00	0.00	
292 min	0.54	1.00	0.23	0.07	-0.02	0.11	0.18	0.06	0.47	0.02	0.07	0.06	0.01	0.03	
369 min	0.52	0.73	0.38	0.11	0.04	0.16	0.27	0.10	0.22	0.01	0.16	0.07	0.00	0.00	

**Fig. 4.** Reactants conversions and selectivities to products upon impulse sulphur addition experiments on Ni5 catalyst (A) no sulphur, (B) after 30 min from injection of 0.011 mol_S/mol_{Ni}, (C) after 30 min from injection of 0.033 mol_S/mol_{Ni}, (D) after 135 min, and (E) after 212 min.

recovered with increased selectivities to CO and methane, and lower to CO_2 with respect to the behaviour in the absence of sulphur. After other 105 min this behaviour was reconfirmed. After this, the two injections of sulphur were repeated. Again deactivation was observed of both ethanol and phenol conversion, actually more severe than in the first injection step performed on the fresh

catalyst. However, by repeating the same procedure as above catalytic activity was again almost totally recovered and kept stable later on for 420 min, always with CO selectivities of 57%, CO_2 selectivity slightly increasing from 22% to 30% and methane selectivity declining from 12% to 9%. Small amounts of acetaldehyde were also observed.

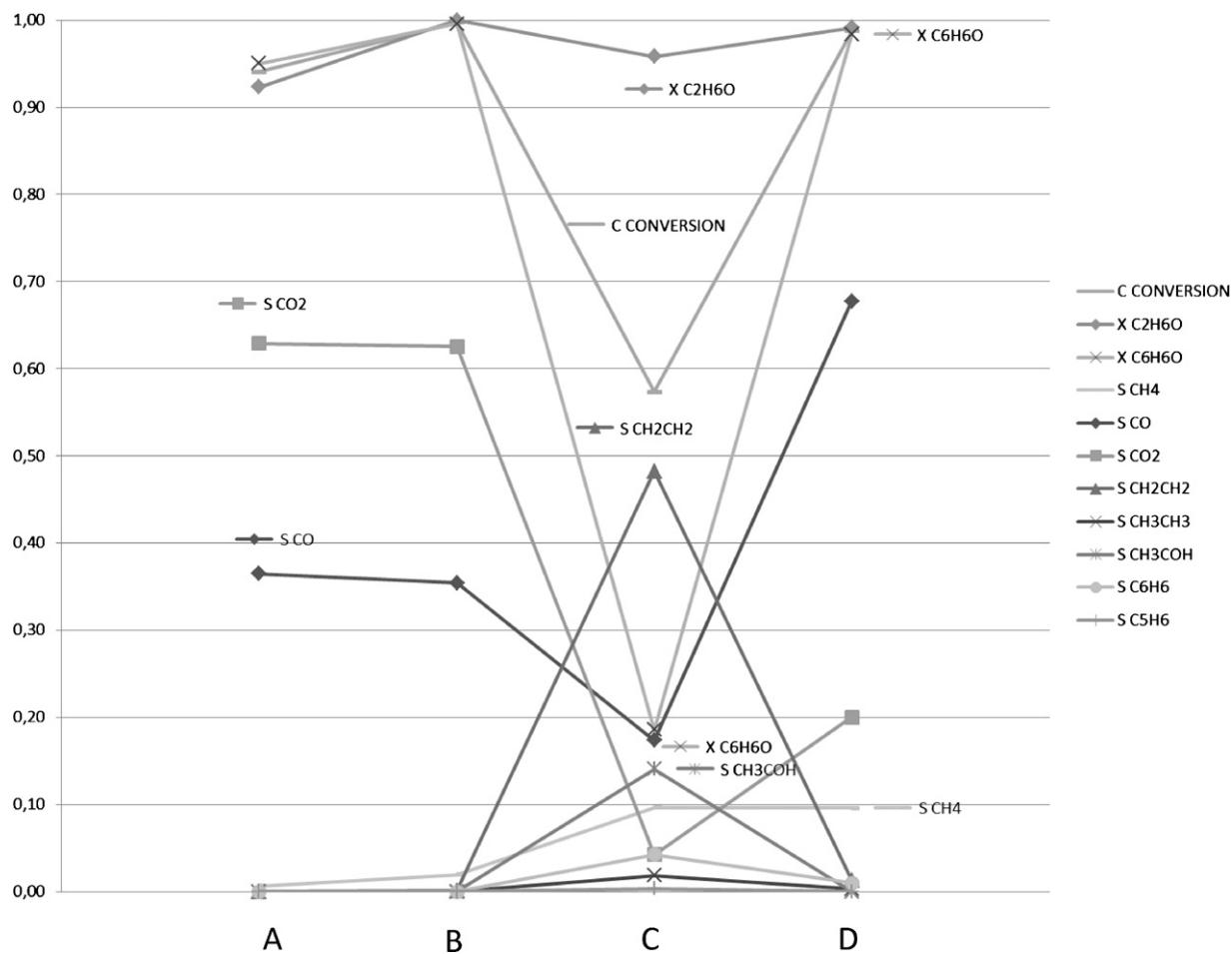


Fig. 5. Reactants conversions and selectivities to products upon impulse sulphur addition experiments on Ni16 catalyst. (A) No sulphur, (B) after 30 min from injection of 0.011 mol_S/mol_{Ni}, (C) after 30 min from injection of 0.033 mol_S/mol_{Ni}, and (D) after 135 min.

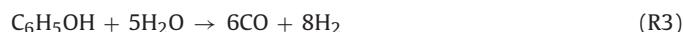
4. Discussion

4.1. Behaviour in sulphur free conditions

The data reported above confirm that SR of ethanol



and of phenol



occurs to a very small extent on the catalyst-free bed, thermally or catalyzed by silica glass or by carbonaceous material, as well as on the alumina bed. Instead, these reactions occur catalyzed by Ni-containing catalysts in the temperature range above 773 K.

Over Ni/Al₂O₃ catalysts ethanol SR is slightly easier than SR of phenol. In fact we find conversion of ethanol to CO_x (with small amounts of methane) larger than that of phenol in the temperature range 773–973 K. However, in agreement with previous studies [29,30] SR of ethanol is competitive with several reactions such as mainly dehydration to ethylene



and dehydrogenation to acetaldehyde



Dehydration to ethylene is clearly catalyzed by “clean” alumina and occurs, in our conditions, in spite of the significant amount of water fed together with ethanol. We verified that, in fact, it is largely favoured thermodynamically even in our conditions. In fact alumina based catalysts have been used for decades to convert bioethanol into ethylene at ca. 573 K [31]. Indeed this reaction is largely predominant at 773 K also on Ni5 but tends to vanish at the same temperature by increasing Ni loading in favour of SR and ethanol dehydrogenation to acetaldehyde. The occurrence of dehydration of ethanol to ethylene could provide evidence of the existence of uncovered alumina also on Ni16 and Ni39. On Ni catalysts this reaction clearly suffers competition with SR. In spite of its endothermic character, this reaction disappears at high temperature over Ni-containing catalysts, due to total conversion of ethanol to SR products.

Dehydrogenation to acetaldehyde (reaction (R6)) occurs even thermally (or catalyzed by silica glass) at 773 K, but is also apparently catalyzed by Nickel. In fact acetaldehyde selectivity at 773 K occurs the more the higher the Ni content in the catalyst. At higher temperatures it almost vanishes, in spite of its endothermic nature, on Ni catalysts due to competition with SR.

Using different conditions and in the absence of phenol, also diethylether, acetic acid and acetone are found as byproducts of ethanol SR [29,30,32]. Here these byproducts are found only in very small amounts. We observe some amount of ethane, always found when ethylene is produced in relevant amounts with hydrogen produced by SR or by ethanol dehydrogenation to acetaldehyde. Interestingly, this is observed also on alumina.

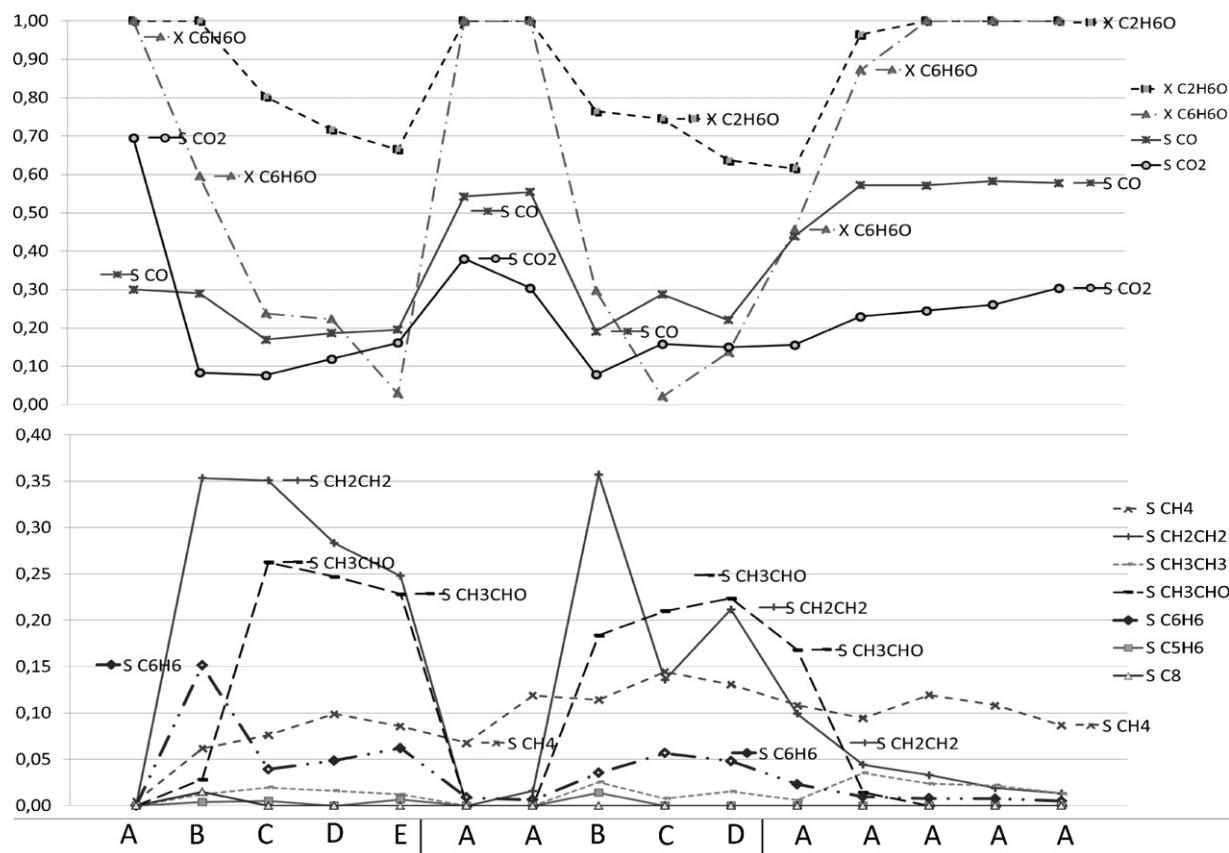
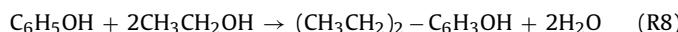


Fig. 6. Reactants conversions and selectivities to products upon impulse sulphur addition experiments on Ni39 catalyst. (A) No sulphur, (B) after 30 min from injection of 0.011 mol_S/mol_{Ni}, (C) after 30 min from injection of 0.033 mol_S/mol_{Ni}, (D) after 135 min, (E) after 212 min. Top: conversions and selectivities to CO and CO₂. Bottom: selectivity to minor products.

As discussed previously [22] the co-feed of ethanol and phenol with steam allowed to reveal that SR catalysts at low temperature can catalyze alkylation reactions



thus producing even heavier compounds from tar components. We find here the production of alkylphenols at 773 K on Ni0, Ni5 and Ni16. Indeed significant yields in alkylphenols are obtained not only with alumina (carbon yields 0.15 at 773 K) but also with Ni containing catalysts, the maximum yields to alkylates (C8 + C10 compounds) being obtained with Ni16 at 773 K (0.22 carbon yield). This suggests that Ni could participate in the catalysis of these reactions. In effect the alkylation of phenol by alcohols in the gas phase is reported to occur with acid/base catalysts such as alumina and magnesia. However an activating effect of transition metals has been reported previously (e.g. in the case of Fe–Mg oxides [33]) and this has been explained suggesting that aldehydes may act as intermediates. This may occur in our case where Ni favours the intermediate formation of acetaldehyde.

As it is evident, ethanol SR is affected by many competitive reactions. On the contrary, phenol SR is more selective, benzene being the only by-product besides alkylates. Benzene is likely produced by hydrodeoxygenation when H₂ becomes available from SR or dehydrogenation (reaction (R6))



The data reported above show that all Nickel containing catalysts are active to convert totally both ethanol and phenol to CO and CO₂ and small amounts of methane when the furnace temperature

is 973 K, actually resulting in a bed temperature of near 943 K. In these conditions in most cases the obtained partial pressure of CO₂ is well higher than that of CO. These data are comparable with those of phenol SR reported by Matas Güell et al. for other supported Ni catalysts [13], taking into account the smaller space velocity we used in our experiments (near 54,000 h⁻¹). The ratio CO/CO₂ might depend on the possible establishment of the water gas shift (WGS) equilibrium:



In Table 8 the results obtained at 973 K are compared with those arising from a thermodynamic calculation. It is evident that the amount of CO₂ obtained with Ni catalysts is higher than that forecast by thermodynamics, while the amount of CO is lower. The calculation of the $\Pi_{\text{WGS}} = P_{\text{CO}_2} \times P_{\text{H}_2} / (P_{\text{CO}} \times P_{\text{H}_2\text{O}})$ reveals in the cases of our reaction products values in the range 2–4, i.e. significantly higher than those calculated for the equilibrium constant K_{P} of WGS. On the other side the ratio $\Pi_{\text{WGS}} / K_{\text{P}(\text{WGS})}$ tends to decrease approaching unity at higher temperatures. This indicates that we are approaching equilibrium mainly from the CO₂-side, the more the higher the reaction temperature. Although two ways can co-exist, producing CO and CO₂ respectively, CO₂ is necessarily the primary product of one of the ways to SR, CO being at least in part produced by the reverse water gas shift reaction. Previously we obtained the same result for ethanol SR on other Ni based catalysts [32].

Methane is produced as a by-product with selectivities generally ≤ 0.06 . The selectivity to methane has a maximum both in the

Table 8

comparison of experimental result with thermodynamic calculation.

Components	yi gas composition at the exit of the reactor (T furnace 973 K)									
	Silica glass	Ni0 IT	Ni0 DT	Thermodynamics	Ni5 IT	Ni5 DT	Ni16 IT	Ni16 DT	Ni39 IT	Ni39 DT
CH ₄	0.002	0.004	0.003	0.001	0.006	0.001	0.001	0.002	0.001	0.000
CO	0.005	0.006	0.005	0.074	0.046	0.059	0.054	0.060	0.056	0.057
CO ₂	0.005	0.003	0.003	0.078	0.102	0.093	0.088	0.091	0.096	0.096
CH ₂ CH ₂	0.006	0.010	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CH ₃ CH ₃	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CH ₃ CHO	0.006	0.007	0.008	0.000	0.000	0.000	0.003	0.000	0.000	0.000
C ₂ H ₆ O	0.026	0.015	0.021	0.000	0.000	0.000	0.001	0.000	0.000	0.000
C ₆ H ₆	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C ₆ H ₆ O	0.018	0.019	0.019	0.000	0.000	0.000	0.001	0.000	0.000	0.000
H ₂	0.023	0.022	0.024	0.321	0.332	0.336	0.315	0.329	0.338	0.339
H ₂ O	0.526	0.534	0.530	0.229	0.213	0.214	0.235	0.218	0.212	0.211
He	0.383	0.380	0.382	0.297	0.301	0.297	0.303	0.298	0.298	0.297
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

increasing and in the decreasing temperature experiment, which suggests that it is mostly formed by decomposition of ethanol



or of its transformation products (acetaldehyde or acetic acid) and is steam reformed at higher temperature. Indeed methane amount at 973 K is well above that allowed by thermodynamics on Ni5 (the least active for SR), while is similar to that allowed by thermodynamics in the other cases. Methane selectivity vanishes at $T > 973$ K. As discussed previously, the production of CO and methane are the factors that stoichiometrically limit the production of hydrogen by phenol and ethanol conversion at $T = 873$ K or above.

The behaviour of the catalysts when the furnace temperature is 873 K shows that Ni39 catalyst is indeed more active as a SR catalyst than Ni16 and Ni5, in fact at this temperature only methane, CO and CO₂ are observed at the exit of the reactor in the decreasing temperature experiment while in the increasing reaction temperature experiment, traces of ethane, ethylene, benzene and phenol are observed in the gas. On the contrary conversion of phenol is largely incomplete in the increasing temperature experiment for both Ni5 and Ni16 and also in the decreasing reaction experiment for Ni5. The behaviour of Ni16 at 873 K is much better in the decreasing temperature experiment than in the increasing reaction temperature experiment: conversion of phenol is 0.25 in increasing temperature experiment and 0.90 in the decreasing temperature one. In both cases ethylene, ethane and benzene and, only in increasing T experiment, acetaldehyde, are observed as byproducts.

The data recorded at 873 K in the decreasing temperature experiments show that the catalysts did not lose, on the contrary gained, activity after several hours on stream. This shows that these catalysts do not deactivate significantly by coking in the timescale of some hours at 873–1023 K and that they may undergo a conditioning process in these conditions. On the other hand, we can note that, in contrast to what is done by most researchers, we did not perform any activation procedure before catalytic tests. In fact our data demonstrate that pretreatment might be not needed in continuous operation (with a remarkable simplification of the startup procedure of the overall plant) or may be performed using the reactor at slightly higher temperatures in the first period of operation. The behaviour of the catalysts at 873 K in the decreasing temperature experiment allows to rank the three catalysts as the function of their catalytic activity in SR, in particular of phenol, as follows: Ni39 > Ni16 > Ni5.

The data show that, in our conditions, hydrogen yields obtained may be very high (85%) Fig. 3. Hydrogen production is obviously not the main goal when catalysts are used to abate tars, converting them into non-condensable compounds. This datum may be relevant when considering our ethanol–phenol mixture as a model

for bio-oil to be steam reformed to produce hydrogen or syngas. In any case, at high temperature, i.e. when organic tar compounds are fully converted, the hydrogen yield is essentially affected by the formation of CO and methane. With fresh catalysts in the absence of sulphur it seems that CO is produced independently from CO₂ or by the reverse water gas shift reaction, which is the more favoured the higher the temperature. Residual methane should depend from the extent of its SR, being mainly produced by decomposition of ethanol or its conversion products, such as surface acetates [30,32].

To propose an explanation for this behaviour we can remind that CO adsorption is strong on reduced metallic Ni, as typically found on most metals where the C–metal bond is dominated by the electron backdonation from the full orbitals of the metal atom to the π^* antibonding orbitals of CO. On the contrary, CO adsorption on cations is much weaker, including on Ni²⁺. However, we proved previously that Ni²⁺ in an oxide environment is very active in oxidizing CO to CO₂ [22]. On the other hand, it seems very likely that the “conditioning” effect we clearly observed starting from the un-reduced catalysts, is associated to a reduction of part of Ni species to metal particles. It is also well known [34] that, in the presence of CO, supported metal particles can reconstruct possibly modifying their size and shape. Thus, “optimal” Ni particles (either in terms of shape, or size, or structure, or even composition, for the possible presence of carbide species) may be formed during conditioning. However, un-reduced dispersed cationic centres may coexist with metal particles [34]. Isolated sites are in fact stabilized in an higher oxidation state by the interaction with oxide supports [35] and are, consequently, possibly retained in the oxidized state by water, as discussed for the Co/Al₂O₃ system [36]. Interestingly, there is today some consensus that oxidized centres are involved in SR of ethanol [37–39].

We can consequently propose, tentatively, that the “conditioned” catalyst can contain “optimal” metal particles, involved in the previous steps of the SR reactions, including C–C bond breaking steps, but also dispersed un-reduced Ni²⁺ sites that can be responsible for the last reaction step, i.e. the oxidation of adsorbed CO to CO₂.

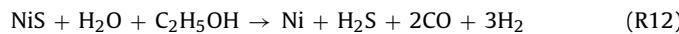
4.2. Behaviour in sulphur containing feed

The experiments performed to evaluate the effect of sulphur on the catalytic behaviour of the Ni containing catalysts show that the catalytic activity of all three catalysts is strongly affected by the presence of 210 ppm (v/v) of sulphur, fed in the form of THT. In all three cases phenol conversion is affected more than ethanol conversion but selectivity of ethanol conversion is strongly modified: in particular ethylene becomes the main ethanol byproducts with the additional formation of acetaldehyde, the higher the Nickel

content. The formation of CO_2 almost vanishes, much more than the formation of CO while benzene, ethane and methane are also found among the products. Apparently the sulphur poisoning of SR activity occurs without concomitant deactivation of the ethanol dehydration sites, likely associated to the residual alumina surface, thus resulting in a shift in the selectivity of ethanol conversion from CO_x to ethylene. The pulse injection experiments show that Ni16 is more resistant to the presence of small amounts of sulphur than Ni5, while the behaviour of Ni39 is apparently comparable with that of Ni16. If we compare the behaviour in terms of amount of sulphur per Ni atom, the results are quite contradictory. In fact Ni16 is the least affected after the first injection (0.011 mol_S/mol_{Ni}), but the most affected after the second injection (0.033 mol_S/mol_{Ni}), when the behaviour of the three catalysts is indeed quite comparable at least as the phenol conversion is concerned.

What is clearly evidenced by the experiments is that, in all cases, the catalytic activity for SR can be essentially recovered by flowing with sulphur free feed. This is an interesting result suggesting that catalyst reactivation procedures might be quite easily performed. It seems that reactivation of sulphur deactivated catalyst in the absence of promoters might not be as difficult as reported for promoted SR catalysts [40], although the nature of the sulphiding molecule (e.g. H_2S instead of THT) may have a role. This activity recovering behaviour is also relevant taking into account that different biomasses can have different sulphur content thus possibly producing variable sulphur concentration in the syngases [14]. Feeding biomasses with very low sulphur content might allow to produce very low sulphur containing syngases allowing the activity of SR catalysts previously deactivated by sulphur to be recovered.

On the other hand the permanence of the CO_2/CO selectivity inversion after sulphur poisoning and regeneration on stream, not relevant for bio-syngas cleaning, provides evidence of some not fully reversible catalyst modification. The inversion in the selectivities to CO and CO_2 , with a strong shift from the CO_2 rich side to the CO rich side of the water gas shift equilibrium, suggests that actually two ways can exist to CO and CO_2 , respectively, and the establishment of the water gas shift equilibrium may be slow in particular in the presence of sulphur. It is possible that CO_x desorption mode, either as CO or as CO_2 , is affected by the presence of sulphur species or by the surface structure modification determined by the previous presence of sulphur in the feed. To explain this behaviour we can propose that flowing with the sulphur-free feed can regenerate the previously sulphided Ni metal particles, possibly with a reaction similar to the following:



However, we supposed above that the CO to CO_2 surface conversion step can involve isolate Ni cations more than metal particles. These sites might be irreversibly poisoned by sulphur possibly in the form of Ni sulphate [41] or because they convert into Ni aluminate NiAl_2O_4 as proposed recently by Yung et al. [42].

5. Conclusions

The data reported in the present paper confirm that Ni/alumina catalyst are effective in complete SR of tars (modelled here by phenol + ethanol mixture) at 873 K, if catalysts are sufficiently charged with Nickel (e.g. 39% Ni with $107 \text{ m}^2/\text{g}$ surface area), CO_2 is largely the main C-containing reaction product and H_2 yield of 85% is obtained. Less loaded catalysts (i.e. 5% Ni) can be very active too, but at higher temperature. These catalysts do not deactivate significantly by coking in the timescale of some hours at 873–1023 K. Starting with unreduced catalysts, a conditioning effect is evident on stream, supposed to be associated to the formation of “optimal” nickel metal particles.

At lower temperatures the SR activity towards phenol + ethanol mixture vanishes, with the appearance of reactions which are catalyzed by uncovered alumina (dehydration of ethanol to ethylene) or by Nickel, like dehydrogenation of ethanol to acetaldehyde and alkylation of phenol to mono- and di-alkyl-phenols. The occurrence of alkylation reactions suggests that SR catalysts, if used at too low a temperature, may catalyze the formation of even larger and less volatile species from tar mixtures, with a negative effect on the syngas quality.

All Ni/ Al_2O_3 catalysts are strongly deactivated by 210 ppm of sulphur working at 973 K. However, catalytic activity could be recovered by flowing with sulphur-free SR feed, although the CO_2/CO product ratio, and consequently also the final hydrogen yield, is permanently altered. It is proposed that the last reaction step, i.e. the oxidation of adsorbed CO to CO_2 previous of its desorption, involves isolated cationic Ni centres that are irreversibly deactivated by sulphur or during the poisoning/regeneration cycle.

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